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SOLID PROPELLANT COMBUSTION MECHANISM STUDIES

Fourteenth Progress Report

For the Period 1 April 1962 to 31 December 1962

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I. INTRODUCTION AND SUMMARY

This report describes research on the mechanism of combustion of solid propellants carried out during the latter part of 1962. The major continuing goals of the research are the direct photographic observation of burning propellant surfaces and the measurement of surface temperatures by thermocouple techniques.

The use of fine thermocouples for probing the temperature of burning propellant strands has been developed further. A number of thermocouple records have been obtained and from these the surface temperature of a burning composite propellant has been found to be near 600° C.

High resolution photomicrographs of burning composite solid propellant surfaces are currently being obtained using equipment described in a previous report (1). A further analysis of the optical system parameters which affect the photographic observations has been carried out and is described below. Some difficulty was experienced due to the emission of radiation from solid particles in the combustion gases which was sufficiently intense to obscure the surface. This problem became limiting at higher pressures which varied with the propellant binder. Nevertheless, interesting photomicrographs have been obtained for three binder systems with results which are described below.

A number of theoretical papers which describe models for the solid propellant combustion process have been published in recent years. These models contain a

variety of assumptions as to the factors governing the combustion process. They meet with varying success in the degree to which they are able to describe accurately the effects of various factors on propellant burning rates. These papers are currently being assessed and compared for the purpose of developing general understanding of the process.

The cooperative study, with Picatinny Arsenal, of propellant burning at very high pressures has been resumed after the repair of the Picatinny burner, but no new results are available at present.

II. THERMOCOUPLE TRAVERSES OF SOLID PROPELLANT FLAME ZONES

Techniques for the casting of fine thermocouples in composite solid propellants have been described in a previous report (2). These techniques and improvements on them have been used to prepare thermocouple-equipped strands of composite and double base propellant for study. The strands thus equipped have been used to gather subsurface temperature profiles of burning solid propellants. From these temperature profiles it has been possible to estimate the temperature at the burning surface for these propellants.

The value of the temperature at the surface of a burning propellant is a uniquely important parameter in defining the combustion mechanism. The surface temperature and the temperature profile in the vicinity of the surface are intimately connected with the state of the material at the surface and the energetics of the chemical reactions which occur in that region. Hugget (3) has discussed several techniques which have been used with varying success to estimate surface temperatures for double base propellants. He reports values for the

surface temperature in the range 250 - 1000°C. although the most probable value is about 300°C.

Friedman (4) has reported attempts to apply thermocouple techniques to the measurement of the surface temperature of composite propellants. Recently, Powling and Smith (5) have described a radiometric technique for characterizing the surface temperature of solid propellants. Their technique has been applied to the measurement of surface temperatures of pressed composite propellant materials. Unfortunately, the radiometric technique is limited to the low pressure regime and estimates of surface temperatures in the more practical pressure regions are not available. In the region of their study they have measured surface temperatures in the 500°C. range.

Two methods have been used to obtain estimates of surface temperature in the current work. The first method is based on the steady state flow of heat from the surface into the burning propellant. Assuming constant thermal conductivity and heat capacity, one may write the steady state energy equation:

$$\lambda \frac{d^2 T}{d x^2} - r \rho c_p \frac{d T}{d x} + \dot{q} = 0$$

where x is the distance along the burning axis, r the burning rate, $\dot{q}$ the enthalpy change associated with the surface reaction and the other symbols have their usual meaning. With a zero heat of reaction and a surface temperature of Ts at x = 0 the equation may be integrated to give:

$$\frac{T - To}{Ts - To} = e^{r \rho C_p x / \lambda}$$

In the range of validity of this expression, a plot of log (T - To) versus x should be a linear with a slope

of $r\rho C_p/\lambda$. At the surface this expression will no longer hold due to changes in the thermal diffusivity. Thus, the deviation of such a plot from linearity would give an estimate of the surface temperature. This reasoning has been applied by Kline, Meinster, Lewis, and Von Elbe (6) in estimating the surface temperature of double base propellants. Its application for both double base and composite propellants in the current work is described below.

Another technique which could be used to disclose the passage of a thermocouple past the burning surface depends upon the electrical insulating character of the propellant and the ionization of the flame gases. In this technique a dual beam oscilloscope is used to read the thermocouple output voltage. At the same time, superimposed on this record is the voltage-time trace from the thermocouple used as an ionization probe. A schematic representation of the instrumentation used to effect this measurement is shown in Figure 1. Using this method, the thermocouple channel should give its normal record of temperature versus time. The probe signal should, however, be discontinuous, the position of its rise corresponding with the emergence of the thermocouple from the propellant surface. This technique is currently being perfected.

A number of temperature-time records for composite and double base propellants have been obtained. In general, the records for double base propellant are much smoother than the corresponding composite records. This behavior is quite reproducible and does not seem to be due to noise, and it must be concluded that the irregularities in the composite records are due to the composite nature of these propellants. Plots of log (T - To) for composite and double base propellants

obtained from voltage-time traces are shown in Figures 2 and 3. As indicated on the illustrations, these plots can be used to obtain estimates of the burning surface temperatures under the conditions described. The results obtained for the double base propellant are consistent with other measurements.

The composite propellant used most extensively thus far is a PBAA propellant containing 70% fine ammonium perchlorate with a mean diameter of 9μ. A surface temperature in the neighborhood of 600°C. has been measured for this propellant at 30 psig in several experiments. Further measurements will be made to corroborate this value.

Plans for the near future include studies of the surface temperature of this propellant at elevated pressures. Other binder systems and, perhaps, other particle size distributions will also be observed by this technique.

III. BURNING SURFACE PHOTOGRAPHY

A. Introduction

Previous reports have described preliminary studies of the influence of various factors on still and motion picture photography of the surface of burning solid propellants (1), (2). The construction of a suitable optical system and optical strand burner and preliminary experimental results have also been described. Efforts during the current reporting period have involved more careful evaluation of the necessary optical system parameters, and minor optical system and strand burner modifications. At the same time, burning surface photography has begun with accompanying photographic interpretation. The program is now in a position

to gather experimental information in a routine fashion and is currently involved primarily with extension of early observations.

B. Influence of Optical System Parameters

A series of photographs of cut, non-burning composite propellant surfaces were taken to permit the evaluation of the capability of the optical system while circumventing the complexities introduced by the combustion process. These photographs were taken to allow judgment of the visual suitability of photographs produced under independently varied magnification, exposure, lens aperture, and film conditions. The major conclusion was that depth of field was, as had previously been thought, a major influence on visual interpretation of burning surface photographs. To delineate more clearly the interplay of the various factors influencing resolution and depth of field, a comprehensive analysis of the optical system operating variables was made.

The major interdependent optical variables influencing resolution and depth of field are magnification, film resolution, optical component quality (resolution), the effective f-stop of the system, and the allowable "circle of confusion." For a perfect optical system (in the geometrical optics sense), film resolution determines the information storage capacity of the film per unit area of a perfectly focused image, and magnification provides a scaling factor between detail on the object and recorded detail on the film. The energy input requirements for the formation of a suitable latent image on the film relate these two variables to the effective f-stop of a perfect optical system.

For a system of necessarily-imperfect optical components, some detail on the film is lost due to aberrations. Because of diffraction effects, the

detail recorded on the film is dependent on effective f-stop and either magnification or focal length. Depth of field may be calculated only by means of an a priori assumption regarding the scale of resolution on the film which constitutes satisfactory image quality (diameter of the "circle of confusion"). It is, therefore, apparent that a mathematical treatment of the optical system resolution and depth of field while capable of dealing objectively the physical parameters of the system requires experimental support due to the subjectivity involved in the final interpretation of photographic results.

With these points in mind, an analysis of a simple, single lens photographic system was carried out to determine depth of field (D) as a function of primary optical system magnification (M_1), minimum resolved scale of object detail (d_m), combined film and optical system resolution (d_{of}), and effective f-stop (F)*. The analysis was based on the following arbitrary but reasonable assumption:

$$d = d_d + d_{of} = M_1 d_m$$

where: d = allowable circle of confusion in image plane

d_d = diameter of point source image due to defraction effect

d_{of} = minimum resolved separation of two separate images on film due to combined film resolution and optical aberration effects.

From this assumption, standard geometrical and physical optics relations (7) may be used to calculate the interdependence of depth of field, resolution, magnification, etc.

*Effective f-stop - $F = (M_1 + 1) f$, for f = nominal lens f-stop.

It is particularly apparent from these calculations that depth of field depends very strongly on resolution requirement ($D \propto d_m^2$) while necessary magnification is less dependent ($M_1 \propto d_m^{-1}$) bearing out the well-known relation:

$$D \propto 1/M^2 \text{ for given } F \text{ (exposure conditions) and } d_{of} \text{ (film-optical system resolution).}$$

It should be noted further that a fundamental limitation exists in the fact that, within the range of d_m reasonably associated with the resolution of small solid propellant oxidizer particles (say, d_m equal 10 to 30 microns), depth of field is of the same order as d_m even for the relatively optimistic assumptions employed in this analysis. This and the previous fact point out the desirability of keeping optical system magnification at a minimum consistent with suitable resolution.

Some other photographic techniques which might relieve the depth of field problem were also considered, but these techniques involved problems and equipment judged impractical at this point.

C. Apparatus

In the light of the preceding discussion, burning strand surface photography proceeded. Photographs of burning surfaces were made at relatively low primary magnification (7X) and at the higher combustion pressures made possible by the availability of the optical strand burner. The relatively low magnification employed allowed the use of a shorter optical system. The previously described two-lens optical system (1) was modified to a single-lens system. Modification of the system included use of a higher-quality enlarging lens (100 mm. Schneider Componon, with a Compur shutter providing flash synchroni-

ization to 1/500 sec. shutter speed) mounted in reverse to insure operation near design condition.

The optical strand burner described previously (1) was also modified slightly. The previous arrangement which involved a purge gas inlet at the bottom of the burner was found to produce an ejector effect which lowered the pressure between the inner chimney and burner pressure body. This pressure decrease promoted a slight leakage of product gases from inside the inner chimney to the annular region between it and the pressure windows. This leakage resulted in a deposition on the inner surfaces of the pressure windows. The new arrangement in which gas is introduced at the top of the burner and flows down through the annular passage precludes such leakage.

The solid angle available for strand lighting is limited due to the narrow slot windows in the existing optical burner. Therefore, without using light sources of greater brightness than those common in commercially-available photographic electronic flash lamps it is not possible to effect an appreciable increase in the light intensity incident on the surface. For this reason a source of rather low energy per flash (30 watt-sec.) is quite suitable, and a small commercial unit of less than 1 msec. effective flash duration has been used. The illumination from this source is comparable to or perhaps slightly greater than that which might be obtained from a well-designed strobing source suitable for cinematographic use. Hence, current single-frame photographic conditions and results are similar to those which might be expected with multiframe photography with considerably more complex light sources.

Test photographs of non-burning, cut-surface propellant samples with films of different speeds

(and resolution) and with varying effective f-stops were made. The results indicated that best combination of resolution and depth of field for 35 mm. photography were obtained with Plus-X film and an effective f-stop of 164 (nominal f/22 at 7X magnification) for the lighting conditions used. This combination has been quite successfully used for numerous photographs. The optical system construction allows use of this thin emulsion, high resolution 35 mm. film for detail photography as well as 4" x 5" cut films and Polaroid films for overall views and synchronization checks. The optical system provides variable magnification for higher resolution photography with limited depth of field. Thus, through variation of both film size and magnification, a wide range of surface photographs is available varying from low resolution large frame pictures of the complete burning surface to small frame, high resolution, high magnification photographs of small details on the surface.

In order to photograph strands burning at elevated pressures, it is necessary to synchronize the shutter and light source with the passage of the propellant surface through the field of view. A photo-electric trigger device was developed to sense the flame luminosity as the burning surface passes the field of view. Its arrangement is as shown in Figure 4. As the burning surface regresses, it is imaged at about 5X magnification by the detector optics on a plane at which is mounted a semiconductive photo-resistor. This photo-resistor, with appropriate amplifier and relay circuit, trips the solenoid-actuated optical system shutter and triggers the light flash. The exposed face of the photo-resistor is approximately 2 mm. in diameter which, in the 5X magnified burning strand image plane corresponds to only

about 400 microns motion of the burning surface. Thus, this trigger device has the capacity for quite reproducible triggering of the optical system shutter. Sensitivity is adjustable to assure that stray radiation does not trip the shutter before the burning surface passes the field of view of the photo-resistor. The sensitivity adjustment also allows for variations in this background radiation from propellant to propellant.

D. Photographs of Burning Strands

The major problem encountered in attempts at burning surface photography was the masking of the burning surface by strong carbon continuum radiation from thermally-emitting carbon particles in the gas phase above the surface. Figure 5a shows a polybutadiene-acrylic acid-ammonium perchlorate propellant burning at 250 psig. The flame luminosity evident in this photograph obscures the burning surface from view. In photographs of the same propellant burning at pressures up to about 100 psig made under identical exposure conditions, the surface can be observed through the flame. This increase in flame luminosity with increasing pressure is particularly evident with PBAA propellants. The observed increase in flame luminosity was paralleled by an increase in soot deposits on the strand burner interior after each run. As pressure is increased, the luminosity seems to appear first in the form of streamers or jets emanating from the entire burning surface. This indicates that the emission is not necessarily to be associated with quenching near the strand edges due to the relatively cold nitrogen purge gas stream. Substitution of air as a purge gas appears to have a negligible effect on reducing this luminosity. Attempts to alleviate this problem by changing oxidizer mass concentration and oxidizer particle size and distribution also failed to yield major decreases in flame luminosity.

Changes in the nature of the fuel binder resulted in a significant reduction in flame luminosity. While polybutadiene-acrylic acid and polyester-polystyrene fuels gave evidence of considerable radiation above 100 psig, a polysulfide propellant allowed views of the burning surface up to almost 500 psig. A photograph of a strand of a polysulfide-ammonium perchlorate propellant burning at 300 psig is shown in Figure 5b. This photograph was made under exposure conditions identical with those used for photograph 5a. Because of the wider pressure range observable with this binder system it was selected for immediate study.

E. Results

Single frame photographs of burning propellant surfaces have been obtained in black-and-white for a polysulfide-ammonium perchlorate propellant with bimodal oxidizer distribution (80% oxidizer; 70% coarse, 30% fine). Figures 6 and 7 showed detailed, enlarged views of the surface from 35 mm. frames taken at 7X magnification on the film and reproduced here after enlargement to 50X.

The following observations are based on a rather small number of photographs and are subject to reinterpretation with continuing photographic efforts:

1. The surface is very heterogeneous, this heterogeneity being of two scales due to the bimodal oxidizer distribution present.

2. Some large oxidizer particles are apparently lying rather free on the burning surface. Fewer appear to be present at higher pressures (say 200 to 500 psig) than at lower (near atmospheric). In almost all cases, a "haze" is apparent in the vicinity of each large particle. That this haze is <u>not</u> self-luminosity accompanying decomposition or reaction was verified by

photographing surfaces under the same conditions but <u>without</u> auxiliary illumination. All such photographs showed little or no image of such haze, indicating that by and large their images in photographs <u>with</u> auxiliary light were formed by reflected not emitted light.

3. A large scale crater-like surface structure is apparent. Small or intermediate bright centers apparently within the crater depression are usually observable along with such individual craters. Within some craters, there is no evidence of bright area whatsoever. In some cases, these local bright areas are fairly distinct, while in others, a haze like that reported above is apparent.

4. The hazy, cloud-like appearance mentioned above is observed to be considerably less predominant at higher pressures. It is considerably less apparent at 100 psig (Figure 7) than at 20 psig (Figure 6). However, the phenomenon appears to be observable up to 500 psig.

5. At low pressure, some free-lying perchlorate crystals show bright spots within an overall haze closely hugging the crystal.

6. Fine-scale particle structure is apparent between craters. It appears to be connected with small perchlorate crystals lying partly or fully exposed but apparently unaccompanied by a small scale equivalent of the craters discussed above in connection with large particles.

On the basis of these observations, it appears that several different modes of surface structure are present in the combustion of polysulfide-bimodal ammonium perchlorate propellants burning at pressures between atmospheric and 500 psig.

First, some large oxidizer particles appear essentially free on the surface. These have also

appeared on early photographs of other propellants. It appears that their presence must be due to fuel pyrolysis at such a rate as to leave large crystals without surrounding binder. If such is the case, it is quite reasonable that, under the action of gravity, these free crystals will "ride" the surface during its regression until finally they are completely consumed. This phenomenon has been observed by other workers (8).

Second, a number of equally-large oxidizer particles appear to pyrolize _faster_ than the fuel binder leaving craters in the surrounding fuel-fine particle oxidizer matrix. It is supposed that the bright spots appearing in these craters are partially-pyrolized perchlorate crystals with their variation in size accounted for by the variation in extent of pyrolysis of the crystals in different craters.

Small particles, though indistinct in the present photographs, indicate less evident crater-like surroundings. This is reasonable considering size influences only, and it is not yet clear to what extent small particles may pyrolize in a different local environment than the larger crystals. Thus, it is particularly evident from the photographs that, at least in the case of large oxidizer particles, a time-unsteadiness of "surface" regression occurs. The extent to which this must be accounted for in burning mechanism theory is not clear _a priori_ and warrants further investigation.

The haze observed to surround a number of large perchlorate crystals is difficult to interpret but is likely to bear on the chemistry of oxidizer pyrolysis at the surface. The cloud-like appearance is not likely to be due to carbon particles formed as intermediate products in the flame. Observation of the haze by reflected light implies a high reflectivity

(low emissivity) for it, whereas carbon particles would be expected to exhibit high emissivities. The chemical nature of this reflecting haze may be made more clear by future color or filtered-light photographs.

F. Future Plans

Plans for the immediate future include color photography to aid interpretation of those details which are apparent but difficult to interpret from high resolution black and white photographs. Following color photography, some efforts may be made in higher magnification, lower depth of field studies of individual burning surface details. The observations will be extended to other propellant systems and higher pressures to such an extent as flame luminosity considerations permit. In particular, propellants with polyurethane fuel binders will be investigated along with propellants with ammonium nitrate and potassium perchlorate oxidizer. Double-base and metalized composite propellants will also be investigated. Since burning surface photography is apparently limited by flame luminosity at higher pressures, strands burning at subatmospheric pressures will also be photographed.

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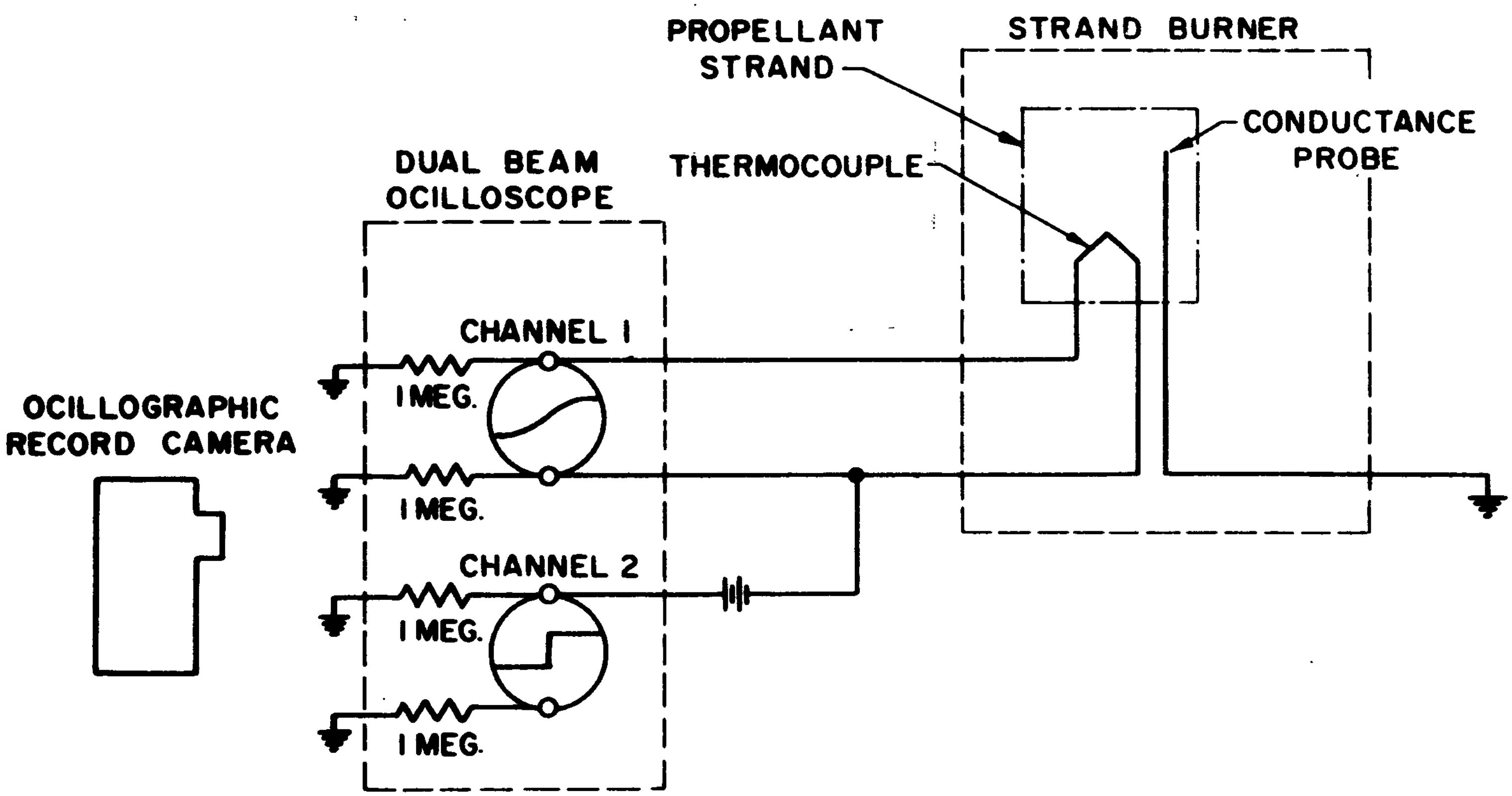
JPR 1572



INSTRUMENTAL SET-UP FOR THERMOCOUPLE TRAVERSES

CHANNEL 1 MEASURES THERMOCOUPLE SIGNAL
CHANNEL 2 MEASURES ONSET OF IONIZATION

FIGURE 1

JPR 1574

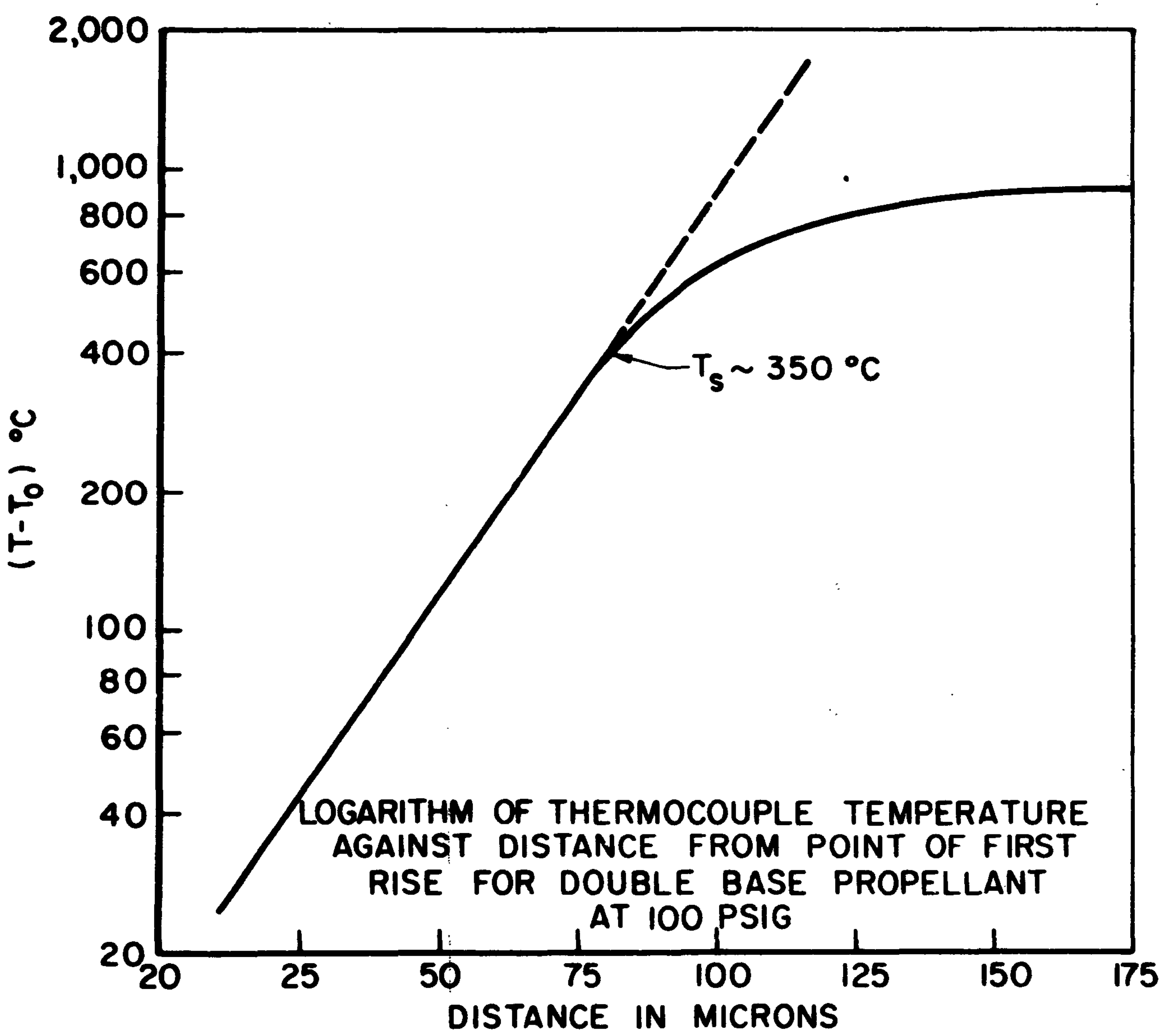


FIGURE 2

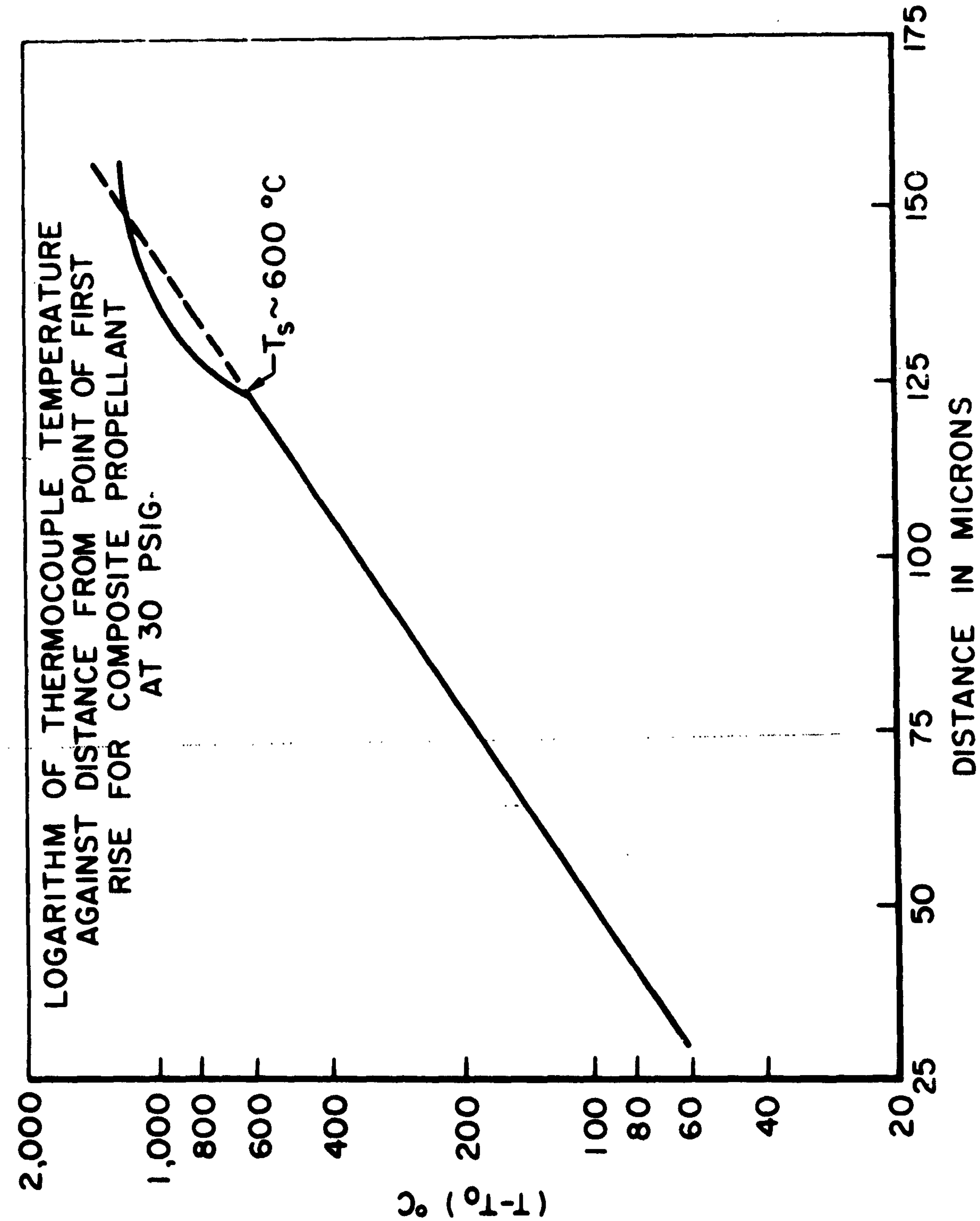


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FIGURE 3

JPR 1551

OPTICAL SYSTEM FOR OBSERVING SURFACE DURING BURNING

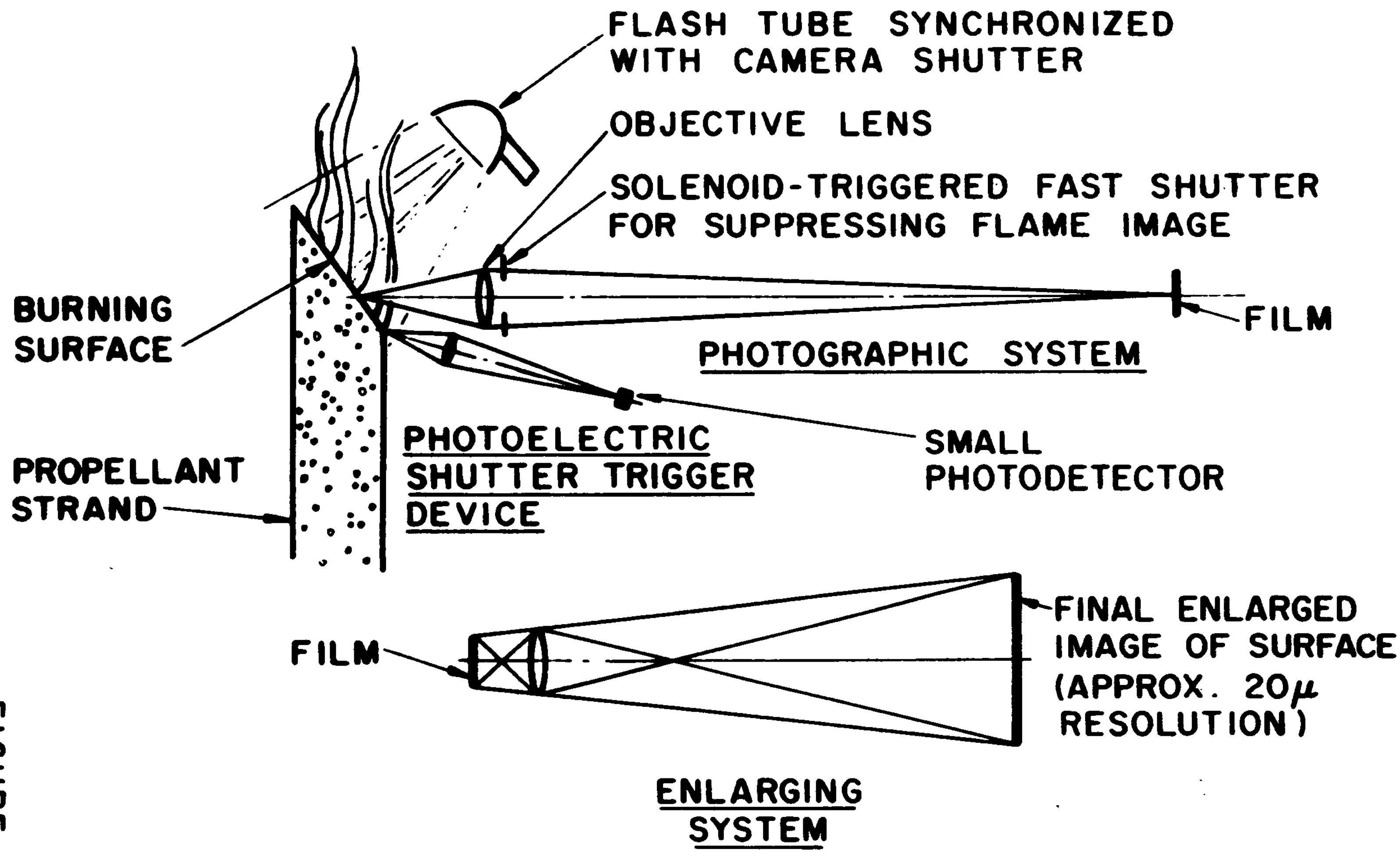
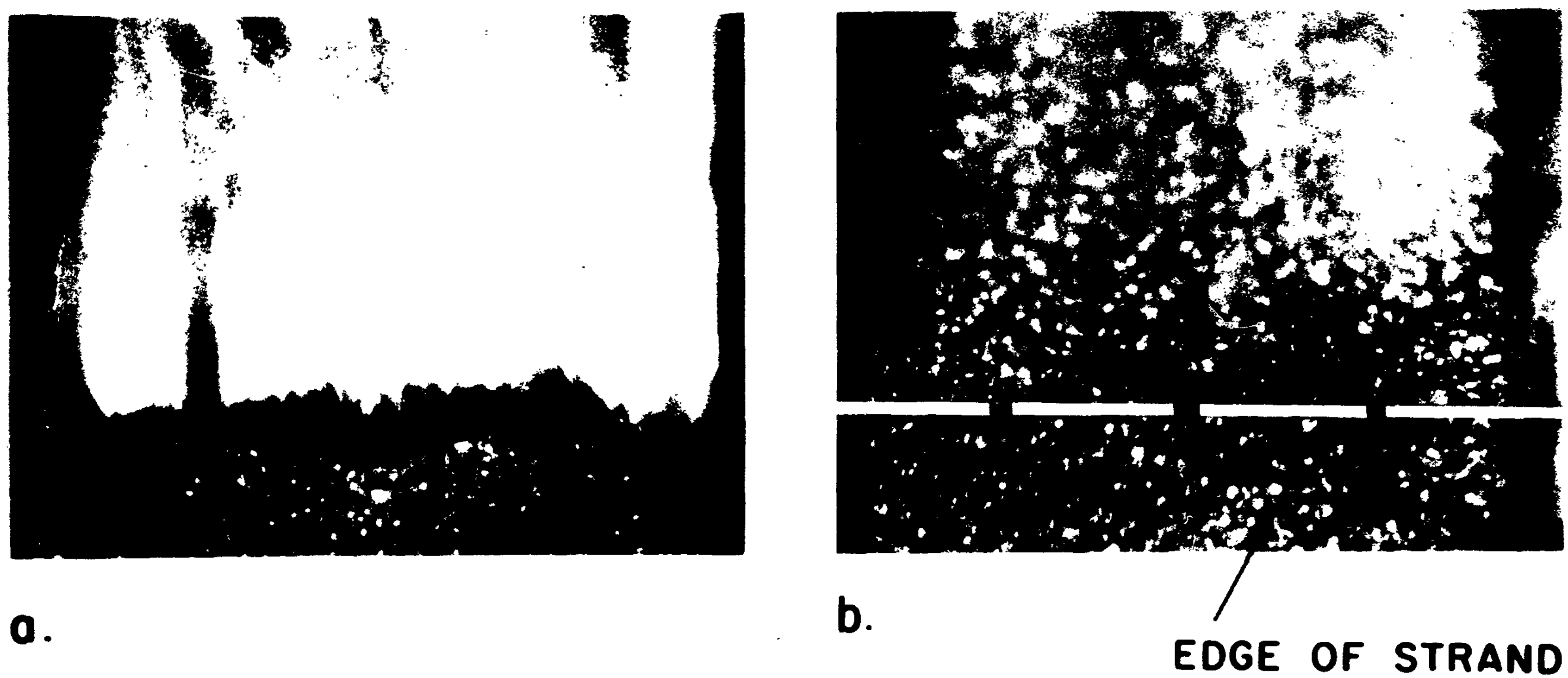


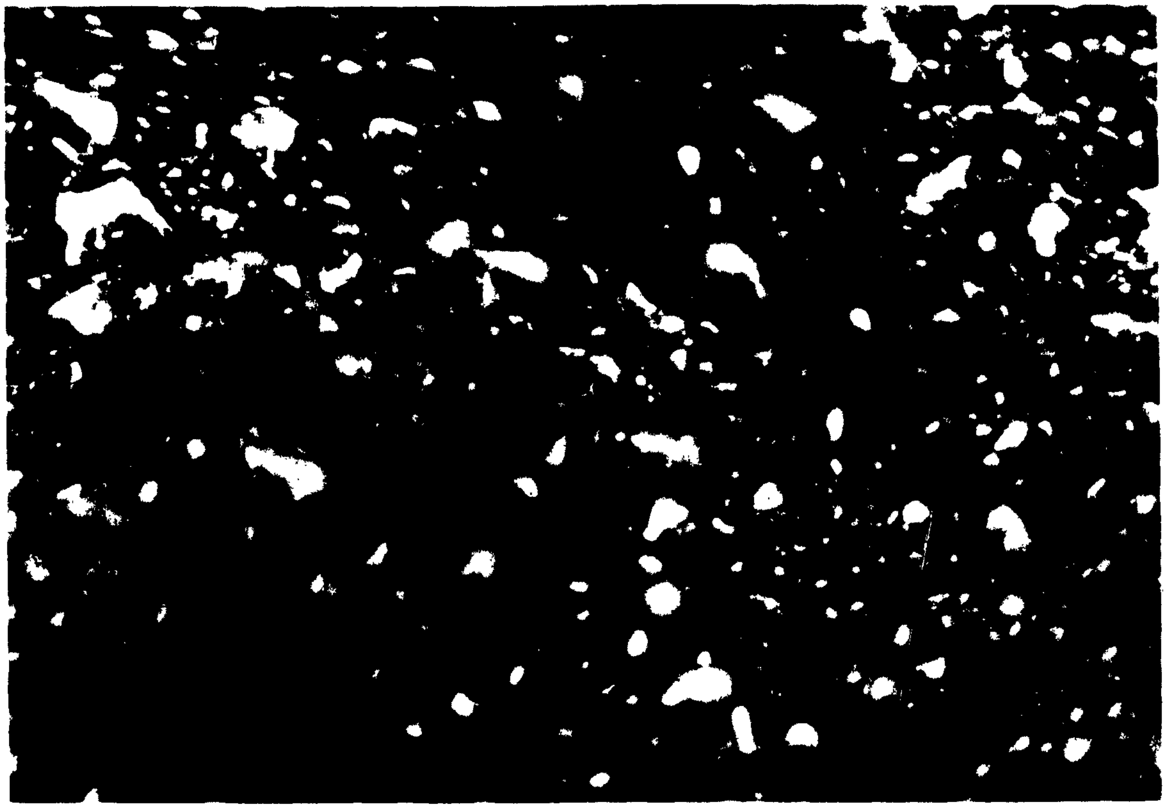
FIGURE 4



a – PBAA PROPELLANT BURNING AT 250 psig

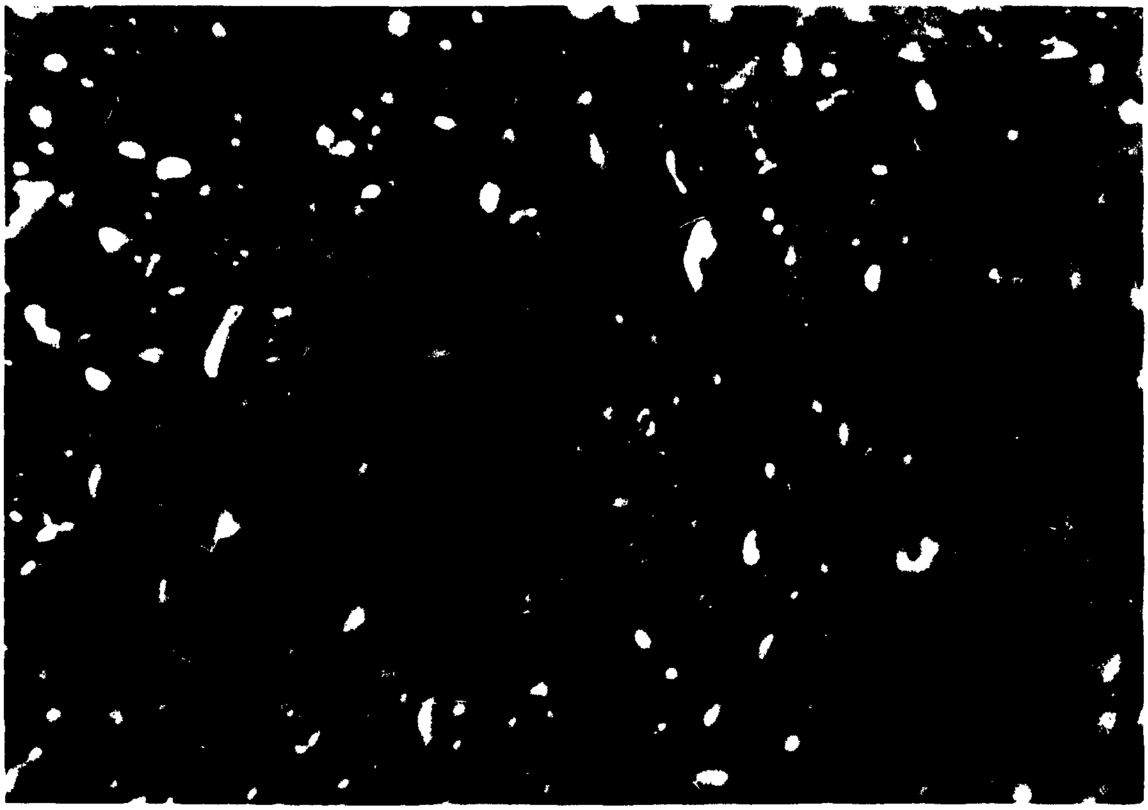
b – LP-3 PROPELLANT BURNING AT 300 psig

FIGURE 5



SURFACE OF POLYSULFIDE - AMMONIUM PERCHLORATE PROPELLANT BURNING AT 20 psig

FIGURE 6



SURFACE OF POLYSULFIDE - AMMONIUM PERCHLORATE PROPELLANT BURNING AT 100 psig

FIGURE 7